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Continuum State Calculations in Atmospheric Physics

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The AHPCRC theory group at Florida A&M University (FAMU) is composed of the following scientists: Professor Charles Weatherford, Professor Herbert Jones, and Assistant Professor Bidhan Saha. The AHPCRC-FAMU theory group also has one graduate student (Mei Dong), one senior undergraduate (Lonnie Mott), and one junior undergraduate (Terrance Dubreus). The group operates a two-processor Silicon Graphics (SGI) Power Challenge, an IBM RISC 6000 workstation, an SGI Indigo2, an SGI Indy, four Macintosh Power PCs, and various other smaller Macintoshes and IBMs. Also used are the CM-5 and CRAY T3D located at the AHPCRC Headquarters in Minneapolis.

The present project has as its objective the calculation of scattering cross sections for constituents of the Earth's atmosphere-this includes electron-molecule, atom-atom, atom-ion, and atom-molecule collisions. A computational technology is being developed which makes efficient use of massively parallel computers. In doing so, some of the techniques of computational fluid dynamics are being adapted to molecular physics and quantum chemistry. These calculations will open the way to large scale modeling of the Earth's atmospheric energy-exchange processes which are important for weather prediction. In addition, the same techniques, with different emphasis, are applicable to the study of electronic aging of materials, particularly cubane derivatives (a high explosive), and for combustion and propulsion studies. A finite element scattering code is being developed which is to be run on the CRAY T3D parallel computer. It features a "hyper-ray" technique wherein the calculation may be partitioned into completely independent pieces which may be executed on different processors simultaneously, with no inter-processor communication required. Then a variational linear combination of the pieces is constructed so as to provide a complete solution to the problem.

The research, to this point, has mainly involved two research topics: electron-molecule scattering and atom-ion scattering.

I. Electron-Molecule Scattering

Electron collisions with molecules are an important secondary energy deposition mechanism by which the sun interacts with the Earth's atmosphere. The solar wind, which consists mainly of highly charged atoms, impacts with the constituents of the Earth's upper atmosphere and liberates free electrons by the process of impact ionization. These electrons are then free to collide with atoms and molecules in the Earth's atmosphere.

One spectacular result of these types of interactions is the aurora borealis or "Northern Lights." The aurora borealis occurs when atoms and molecules (principally atomic oxygen and molecular nitrogen) are ionized by electron and atomic ion impact. Subsequent electronic excitation occurs during the capture of free electrons, with the further creation of the Northern Lights during deexcitation to the ground state of the atom or molecule. Thus, the ionic makeup of the Earth's atmosphere (concentrated principally in the ionosphere, which begins at about 60 km above the Earth's surface) is very important in understanding the energy exchange mechanisms within the Earth's atmosphere. An important direct effect of the ionosphere is on radio communication.
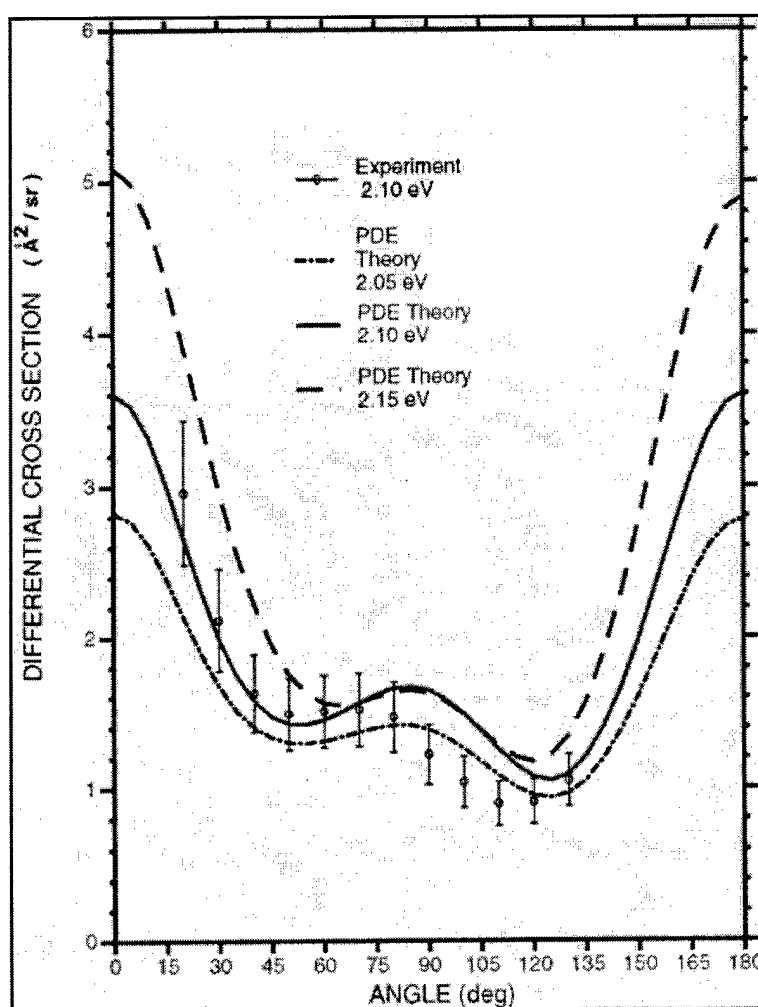

Figure 1. Angular distribution in vibrational elastic scattering for electron-nitrogen molecule collisions, present theory and experiment. Theexperiment is that of Buckman et al. (see Ref. 1).

To give a little background information on this phenomenon, a molecule is much more complicated than an atom because of the various types of excitations which may occur. In an atom, excitation of the electronic bound states are the only possible modes. In a molecule, not only are electronic excitations possible, but rotational and vibrational excitations of the geometrical nuclear states are possible. One key aspect of the calculations we are performing is that they are ab initio. We know exactly the forces (Coulomb, electron-exchange, correlation, and polarization) and the dynamical equations (coupled Schrödinger equations) which govern the collision processes. We also use well-controlled numerical approximations. This means that at each stage of the computation, we have the capability, at least in principle, to refine the results to an arbitrarily high accuracy. Whenever possible, we attempt to compare our calculations quantitatively with experiment. When we place our calculated results on a graph with an experiment, we are frequently in a position to claim equal or superior validity. As an example, consider Figure 1, from Ref. 1, wherein we present an angular distribution of electrons elastically scattered from nitrogen molecules at three different calculated energies (2.05, 2.10, and 2.15 electron volts (eV)), compared with three different experiments (refer to Ref. 1 for citations for the experiments) at 2.10 eV. The excellent agreement with the experimental results is clearly evident.

We have performed calculations on N2, H2, and CH4. So far we have calculated total, elastic, and vibrational excitation cross sections. We intend to continue with calculations of inelastic electronic excitation and simultaneous electronic- vibrational excitation. We also intend to calculate ionization and dissociative attachment cross sections.

The same techniques discussed above are also capable of calculating electron interactions with cubane molecules and their derivatives. Cubane (C8H8) was first synthesized in 1964 at the University of Chicago. It has an Oh point group and a standard heat of formation of approximately 144.5 kcal/mol with a strain energy of about 166 kcal/mol. This is a strain energy of about 14 kcal/mol per carbon-carbon bond.

A new technique for the synthesis of cubane and its derivatives has been discovered by Bashir Hasemi at Geo-Centers Inc., Lake Hopatcong, N.J., such that the usefulness is likely to rapidly expand. The military is interested in polynitro-substituted cubane because of its potential use in high explosives. Interestingly, a dipivaloylcubane compound has been found to have use as an anti-HIV (human immunodefiency virus) agent.

An aspect of the present research has as its aim to study the stability of cubane and certain of its derivatives (tetranitrocubane, with four NO2 groups, at opposite vertices of the carbon cube, and octanitrocubane, with eight NO2 groups at each of the eight vertices of the cube). In particular, we are

assessing the stability of cubanes in interaction with low-to-intermediate energy electrons (0-20 eV), with respect to certain processes that have been called electronic aging. Thus, we are determining to what extent the cubanes are subject to loss of stability when in the presence of continuum electron interactions. We are looking at the elastic and total cross sections for electron scattering in the fixed-nuclei approximation and calculating the effective carbon-carbon vibration cross sections using body-frame close-coupling. Because we solve the continuum Schrodinger equation as a partial differential equation, we are able to consider scattering from an arbitrarily shaped atomic cluster, with numerically generated adaptive grids.

II. Ion-Atom Scattering

A theoretical investigation of alignment and geometrical effects in inelastic collisions of low-Rydberg atoms with rare-gas atoms and molecules is being conducted in this project. The domain of collisional processes involving excited atoms is nearly limitless in variety and complexity. The collision dynamics and the cross sections and other observable parameters (such as correlation, polarization, etc.) usually reflect details that are characteristic of a particular pair of collision partners and initial states. At low collision velocities (v << 1 a.u.), intermediate, near-adiabatic, quasi-molecular states that are quite system-specific, largely determine the physical development of the system during the collision.
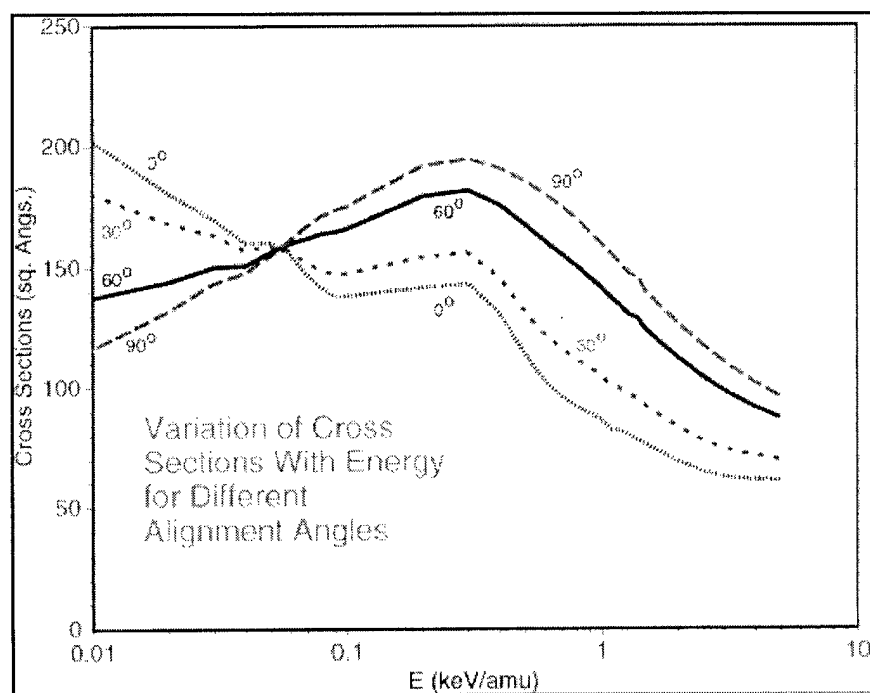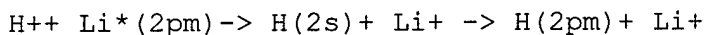

Figure 2. Variation of the cross section for the formation of H(2p), in collisions of protons with excited lithium atoms, as a

function of collision energy, for different alignment angles (see Ref. 2).

While we calculate cross sections-differential and total-and other correlation/polarization collision parameters for the purpose of direct comparisons with measurements and for applications, we give special attention to the study of the dependence of these cross sections and collision parameters on geometry (size and shape), orientation, and alignment of the initial state of the target. We are using semi-classical, close-coupling methods for all but the lowest-energy studies. The time-dependent physical quantities, e.g., transition amplitudes and electronic charge density, provide information on the evolution of the collision dynamics. Our method is the molecular orbital (MO) approach in which the total system wave function is expanded in terms of electronic MO wave functions, augmented by electron translation factors to get rid of the artificial long-range couplings by satisfying the correct scattering boundary conditions. We are currently investigating systems like excited alkali atoms colliding with rare-gas atoms or closed-shell diatomic molecules (such as H2, Li2, N2, etc.). We are also studying charge transfer in ion-atom and ion-molecule scattering in this project.

As a specific example, consider the reaction (see Ref. 2):

H++ Li*(2pm)-> H(2s)+ Li+ -> H(2pm)+ Li+

Charge-transfer cross sections, from the initially aligned 2p-state of lithium atoms, with protons have been calculated in the 10 eV to 5 keV/amu energy region. The dependence of the cross section for the formation of the first excited n =3D 2 1 states of the hydrogen atom, on the orbital geometry and the alignment of the initial state have been calculated. The cross sections are sensitive to the variation of the spatial alignment of the electron charge distribution. The cross section decreases with increasing initial alignment at lower energies, and at higher energies, the situation is reversed. This is illustrated in Figure 2. At an energy of E =3D 0.05 keV/amu, the cross section is isotropically aligned. At this energy, the cross section is the same for both of the initial states $\sum$ and 11 $\cdot\cdot$ $\frac{C\rho_i\cdot}{k}$ The orientation of the excited H(2p) orbital resulting from electron capture has also been calculated.

The study of the dependence of the cross shape, orientation, and alignment of the initial state of the target has drawn considerable attention in recent years. It is experimentally possible to spatially align and orient the electronic charge cloud of an initially excited atom to study this dependence for various charge transfer processes. In surface scattering, a prior knowledge of these effects is very crucial.

References

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2. Bidhan C. Saha and Charles A. Weatherford, "Electron Capture From Alkali Atoms by H+ at Low Energies," accepted for publication by Theochem.